Organic and Biological Chemistry

Long-Range Electron Paramagnetic Resonance Coupling Constants in Aliphatic Semidiones. A Theoretical Treatment

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Abstract: The extended Hückel theory has been applied to the calculation of long-range hfsc's in semidione radical anions and is shown to give good agreement with the experimental results. Several bicyclic aliphatic semidiones have been used to illustrate the method and to investigate the effects of changes in geometry and substitution. Calculations on a number of neutral alkyl radicals point to the qualitative rules for maximum long-range interaction. Good agreement could not be attained for the hfsc ratios of *cis*- and *trans*-butane-2,3-semidione.

Long-range hyperfine (hf) interaction in epr spectra has been well documented,[2–5] especially in rigid systems where the geometric requirements have been noted most frequently,[5] and it is desirable to apply certain theoretical approaches to these systems in order to aid in the interpretation and assignment of long-range hf splittings. Several successful attempts have been made to calculate spin densities and to correlate these with the observed hf splitting constants (hfsc) for α-protons[6] and β-protons;[7–14] however, there appear to be very few treatments of more distant interactions. The extended Hückel (EH) theory of Hoffmann and Lipscomb[15] which includes nonneighbor interactions appeared to us to be applicable to the question of long-range hf interactions and their geometric requirements. The EH theory has met with considerable success in dealing with conformational and stereochemical phenomena[16–19] and has been successfully applied by Petersson and McLachlan[20] to the calculation of hfsc's for a series of neutral radicals. Most recently, Drago and Peterson[21] have obtained excellent agreement for several radicals and radical anions using an EH treatment.

A large number of long-range hf interactions have been observed[2,3,5,22–24] in readily accessible semidione radical anions, and because their identity is well established, they were selected for this study. Our object was to apply the EH theory to semidiones and determine its usefulness in predicting long-range hfsc's and the effects of geometry and substitution on these interactions.

Extended Hückel Approach

Slater[25] 2s and 2p orbitals for carbon and oxygen and the Slater 1s orbital for hydrogen were used as the basis set for a linear combination of atomic orbitals (AO's) to build up the required molecular orbitals. All-neighbor

$$\psi_i = \sum_j c_{ij}\phi_j \qquad (1)$$

and nonneighbor overlaps (S_{ij}) were calculated[26] and were also used in the Wolfsberg–Helmholtz[27] approximation for the off-diagonal resonance integrals

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij} \qquad (2)$$

where H_{ii} is the valence-state ionization potential of orbital *i*. The H_{ii} values used were essentially those of Skinner and Pritchard,[28] (H_{1s}) = -13.6, (C_{2s}) =

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(2) G. A. Russell and K.-Y. Chang, *J. Amer. Chem. Soc.*, **87**, 4381 (1965).

(3) G. A. Russell, K.-Y. Chang, and C. W. Jefford, *ibid.*, **87**, 4383 (1965).

(4) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967).

(5) G. A. Russell, G. Holland, K.-Y. Chang, and L. M. Zalkow, *Tetrahedron Lett.*, **21**, 1955 (1967).

(6) A. Carrington, *Quart. Rev.* (London), 17, 67 (1963), and references cited therein.

(7) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

(8) D. B. Chestnut, *J. Chem. Phys.*, **29**, 43 (1958).

(9) P. G. Lykos, *ibid.*, **32**, 625 (1960).

(10) A. D. MacLachlan, *Mol. Phys.*, **1**, 233 (1958).

(11) P. Nordio, M. V. Pavan, and G. Giacometti, *Theor. Chim. Acta*, **1**, 302 (1963).

(12) F. J. Adrian and M. Karplus, *J. Chem. Phys.*, **41**, 56 (1964).

(13) W. T. Dixon, *Mol. Phys.*, **9**, 21 (1965).

(14) N. M. Atherton and A. Hinchcliffe, *ibid.*, **12**, 349 (1967).

(15) (a) R. Hoffmann and W. Lipscomb, *J. Chem. Phys.*, **36**, 2179 (1962); (b) R. Hoffmann, *ibid.*, **39**, 1397 (1963); (c) R. Hoffmann, *ibid.*, **40**, 2474 (1964); (d) R. Hoffmann, *ibid.*, **40**, 2478 (1964); (e) R. Hoffmann, *ibid.*, 40, 2488 (1964).

(16) H. Fujimoto and K. Fukui, *Tetrahedron Lett.*, 5551 (1966); K. Fukui and H. Fujimoto, *ibid.*, 4303 (1965).

(17) W. C. Herndon and L. H. Hall, *Theor. Chem. Acta*, **7**, 4 (1967).

(18) J. M. Sichel and M. A. Whitehead, *ibid.*, **5**, 35 (1966).

(19) H. Cambron-Bruderlein and C. Sandorfy, *ibid.*, **4**, 224 (1966).

(20) G. A. Petersson and A. D. McLachlan, *J. Chem. Phys.*, **45**, 628 (1966).

(21) (a) R. S. Drago and H. Peterson, Jr., *J. Amer. Chem. Soc.*, **89**, 3978 (1967), adopted the logical extension of using charge-adjusted valence-state ionization potentials and Slater exponents, iterating to self-consistency, and obtaining the hfsc's by considering the contributions from all AO's. (b) Preliminary indications are that slightly better agreement does result by considering the contribution from all orbitals in the molecule; however, in most of the semidiones, particularly those involving long-range couplings, these errors appear to be small.

(22) E. R. Talaty and G. A. Russell, *ibid.*, **87**, 4867 (1965).

(23) E. R. Talaty and G. A. Russell, *J. Org. Chem.*, **31**, 3455 (1966).

(24) G. A. Russell, E. R. Talaty, and R. Horrocks, *ibid.*, **32**, 353 (1967).

(25) (a) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930). (b) The following Slater exponents were used: C = 1.625, O = 1.275, H = 1.00. It has been pointed out[20] that the relative sizes of the coupling constants are virtually unaffected by changes in the hydrogen Slater exponent

(26) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(27) M. Wolfsberg and L. Helmholtz, *ibid.*, **20**, 837 (1952).

(28) H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

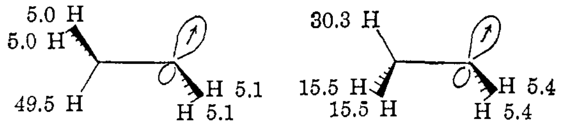

Figure 1. The effect of conformation on a_β^H in the nonplanar ethyl radical.

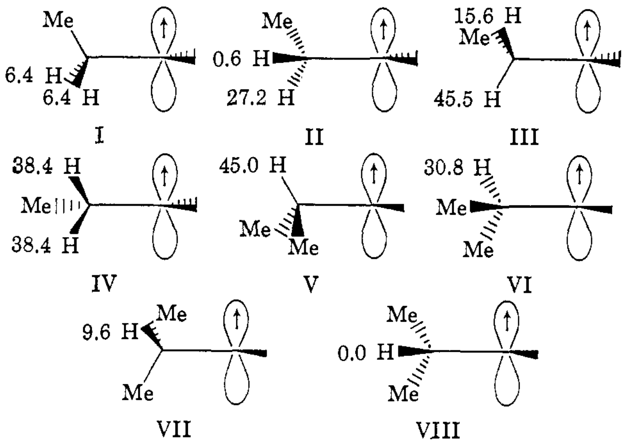

Figure 2. The effect of β substitution on a_β^H. The coupling constants of the β hydrogens are given in gauss and the conformation of the methyl hydrogens is assumed not to affect greatly the value of a_β^H.

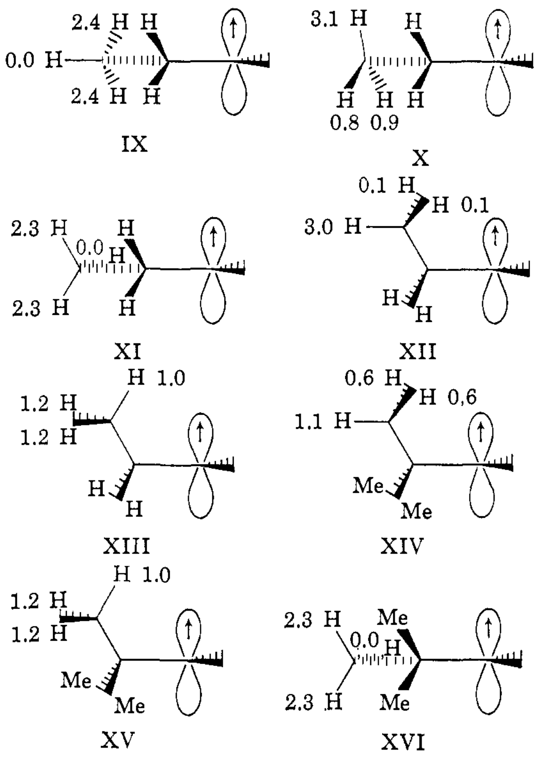

Figure 3. The effect of conformation and β substitution on a_γ^H.

−21.4, $(C_{2p}) = -11.4$, $(O_{2s}) = -35.3$, and $(O_{2p}) = -17.8$ eV. The value of K in eq 2 was 1.75 as discussed by Hoffmann.[15b] The values for the energies and coefficients were obtained in the same manner as outlined by Hoffmann from the secular determinant $|H_{ij} - ES_{ij}| = 0$. The proton couplings were calculated from the coefficients (c_u) of the H_{1s} AO in the molecular orbital (ψ_u) containing the unpaired electron using the expression[20] where only the H_{1s} contribution to the first-order Fermi contact term[29] was considered.[21b]

$$a^H = -{}^{16}/_3 \pi g_H \beta_H c_u^2 \phi^2(H_{1s})$$

Evaluation of this expression leads to $a^H = 878c_u^2$ G.[30]

Results and Discussion

While we have resolved to limit this study to semidiones, we feel that it is instructive to compare the results for some simple radicals of arbitrarily fixed geometry to see if our results conform to the known stereochemical relationships. All carbon–carbon bond lengths were 1.54 Å; carbon–hydrogen, 1.09 Å; bond angles 109.5° (sp^3 carbon) or 120° (sp^2 carbon). All radicals were oriented in the reference framework such that there was always a high spin density in the p_z orbital located at the "radical center"; in this way the molecular orbital containing the unpaired electron was easily recognized. This method led to consistent results and was preferable to making the assignment on energy considerations alone, particularly in the larger bicyclic systems.

Alkyl Radicals. A study of different conformations of the ethyl radical showed that the EH theory gave agreement with the Heller–McConnell equation.[31]

$$a^H = A + B\rho \cos^2 \theta$$

Excellent agreement was obtained for the angular dependence; A was found to be zero while B was 42.3 G. The reported value[32] is 53.7 G. Because spin polarization is neglected in the EH treatment, $a_\alpha^H = 0$, but in the saturated semidiones with no α hydrogens, we feel that this approximation will lead to only minor discrepancies. To illustrate the effect of nonplanarity at the trivalent carbon, values of a^H were calculated for two conformations of a nonplanar ethyl radical in which both carbons are assumed to be sp^3 hybridized. These results are shown in Figure 1. The effect of alkyl substitution at the β carbon is illustrated in Figure 2. The results suggest that a^H is dependent on β substitution as well as on the dihedral angle (for example, compare conformations I, III, and IV where the dihedral angle is 60°). The weighted[33] average for a_β^H for the n-propyl radical is 20.4 G.

From the calculations, it is readily apparent that spin density appears at the γ hydrogens and is approximately the correct order of magnitude.[32] The effect of conformation and β substitution in the propyl radical is shown in Figure 3. As anticipated, a local maximum is observed in conformations XII and XIV corresponding to the W-plan arrangement, and the larger coupling in XIII and XV may be regarded as "through-space" interactions. Fessenden and Schuler found that for the propyl radical at −180°, $a^H = 0.69$ G (2 H) presumably due to IX, while at −145°, $a^H = 0.38$ G (3 H) assignable to a freely rotating methyl (IX, X, and

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(29) E. Fermi, *Z. Physik*, **60**, 320 (1930).

(30) This evaluation was made using a Slater exponent of 1.20, a value which is indicated by SCF calculations.[21a]

(31) H. C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

(32) R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963), report $a_\beta^H = 26.87$ G for a freely rotating methyl group in the ethyl radical. Since $\cos^2 \theta = {}^1/_2$, $B\rho$ is taken to be twice this value.

(33) Conformations I and IV were assigned weights of 2, conformations II and III, weights of 4.

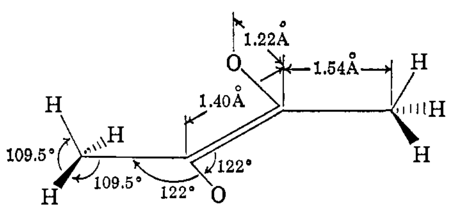

Figure 4. The bond angles and bond lengths assumed for *trans*-butane-2,3-semidione.

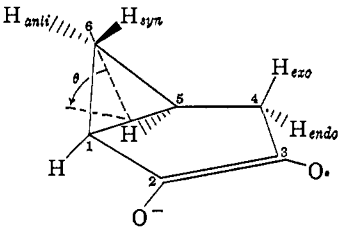

Figure 5. The geometry and numbering for bicyclo[3.1.0]hexane-2,3-semidione.

XI). Our results predict that the latter value should be 67% of that for the former, in good agreement with the observed value of 55%.

The Semidiones. In this field we were first interested in looking at one of the simpler members, butane-2,3-semidione. As our calculations were necessarily based on fixed geometries, we calculated the hfsc's for several conformations and averaged the results. For *trans*-butane-2,3-semidione, the four carbon and two oxygen atoms were assumed to lie in the same plane and the bond angles and bond lengths were as shown in Figure 4. These values are essentially those found for biacetyl[34] except for the CO–CO bond. We consider that in semidiones this bond is probably shorter than in the diketone as the calculated π-bond orders are 0.400 and 0.037, respectively. This increase in bond order we estimate to be associated with a decrease in bond length of about 0.07 Å by analogy with the published[35] bond order–bond distance relationship.

The coupling constant calculated for the freely rotating methyl group in *trans*-butane-2,3-semidione is 10.0 G compared with the experimental[36] value of 5.60 G. For the *cis* isomer, the radical was again assumed to be planar with the same bond angles and bond lengths. This geometry led to a calculated hfsc of 9.8 G, essentially the same as for the *trans* isomer. Experimentally[36] the hfsc is 7.0 G. It has been reported[37] that tiglic acid (possessing *cis*-methyl groups on a double bond) is nonplanar presumably due to methyl–methyl repulsions causing a twist of approximately 4° about the C=C double bond. Twisting a *cis*-semidione model as much as 10° does not cause a significant change in our results, however. In bicyclo[2.2.2]octane-2,3-dione the two carbon–oxygen bonds have been found[38] to be at an angle of 70.5° to one another while our model assumed an angle of only 64°. To examine the effect of such a bond angle change we increased the relevant angle to 70°, but this also had very little effect on the hfsc. Failure to obtain agreement in this particular case appears to be due to the approximation of considering only the H_{1s} contribution to the coupling constants.

Rigid Bicyclic Semidiones. Whereas bicyclic systems are relatively rigid and several precise[39–44] studies of their geometry have been made, there are no data available for semidiones or even for the relevant diketones. Because of the approximate nature of these calculations we have generally taken the geometries calculated by Wilcox,[45] making the obvious changes necessary to convert his values for the semidiones. Where experimental data are available, they are in close agreement with the calculated values. Using these geometries as a basis, variations were made in several bond angles in order to view the trends in the results. No attempt was made to find the "best" geometry as the accuracy of the method does not justify this. Generally, for all bicyclic systems studied the basis geometries are founded on the following rules: C–C bond lengths are 1.54 ± 0.03 Å;[46] CO–CO bond lengths are 1.40 Å; C=O bond lengths are 1.22 Å; H–C–H angles in $-CH_2-$ are 111°; for methine hydrogens all C–C–H bond angles were equal; and the angle between the two carbon–oxygen double bonds was 70°.

Bicyclo[3.1.0]hexane-2,3-semidione. The geometry and numbering is as shown in Figure 5. The five-membered ring carbon atoms and the two oxygen atoms were assumed to lie in the same plane and the internal bond angles were obtained by assuming the minimum total deviation in all bond angles from the preferred value. Two models were considered: $\theta = 65°$ and $\theta = 75°$, and the results are shown in Table I. Quite obviously the use of $\theta = 65°$ leads to much better agreement with experiment than does $\theta = 75°$. There does, however, appear to be a reversal of spin densities at the 5- and 6-hydrogens. This is presumably due to the assumption of a planar five-membered ring.

Table I. Observed[a] and Calculated Coupling Constants for Bicyclo[3.1.0]hexane-2,3-semidiones

Position	1	4-*exo*	4-*endo*	5	6-*anti*	6-*syn*
Unsubstituted						
Obsd	4.0	7.86	14.9	0.8	4.0	0.8
Calcd	7.6[b]	9.4	16.3	5.0	1.0	0.1
	5.0[c]	12.9	22.6	7.0	2.5	0.0
6,6-Dimethyl						
Obsd	5.1	7.6	14.6	0.9	0.45[d]	0.0
Calcd	7.9[b]	10.4	17.0	4.3	1.9[e]	1.3[e]

[a] G. A. Russell, P. R. Whittle, and J. M. McDonnell, *J. Amer. Chem. Soc.*, **89**, 5515 (1967). All values are in gauss. [b] Using $\theta = 65°$. [c] Using $\theta = 75°$. [d] $a_{CH_3}{}^{H}$, three equivalent hydrogens observed. [e] Average value for one conformation only.

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(34) J. E. LuValle and V. Schomaker, *J. Amer. Chem. Soc.*, **61**, 3520 (1939).

(35) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 165.

(36) G. A. Russell and R. D. Stephens, *J. Phys. Chem.*, **70**, 1320 (1966).

(37) A. L. Porte and J. M. Robertson, *J. Chem. Soc.*, **817**, 825 (1959).

(38) H. Krieger and J. J. Lindberg, *Suomen Kemistilehti*, *B*, **33**, 117 (1960).

(39) A. C. McDonald and J. Trotter, *Acta Crystallogr.*, **18**, 243 (1965); **19**, 456 (1965).

(40) N. C. Baenziger, J. R. Doyle, and C. Carpenter, *ibid.*, **14**, 303 (1961).

(41) H. G. Norment, *ibid.*, **18**, 627 (1965).

(42) F. R. Ahmed and E. J. Gabe, *ibid.*, **17**, 603 (1964).

(43) T. N. Margulis, L. Schiff, and M. Rosenblum, *J. Amer. Chem. Soc.*, **87**, 3269 (1965).

(44) W. H. Grant and J. C. Speakman, *Acta Crystallogr.*, **15**, 292 (1962).

(45) C. F. Wilcox, *J. Amer. Chem. Soc.*, **82**, 414 (1960).

(46) Deliberate variation of bond lengths over this range did not cause a significant change in results.

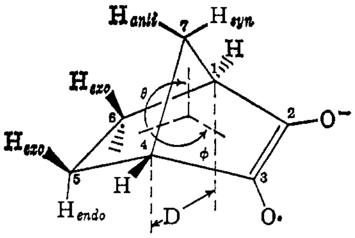

Figure 6. The assumed basic geometry and numbering for bicyclo[2.2.1]heptane-2,3-semidione.

If the 2-carbonyl group were below the plane of the ring the calculated values would most probably be in closer agreement with experiment. It is significant, however, that the assumption of a planar five-membered ring does lead to approximately correct H_{exo}/H_{endo} hfsc ratios at the 4 position. In the 6,6-dimethyl-substituted radical, the $a_{CH_3}{}^{H}$ are predicted in the correct order, but their absolute values are too great.

Bicyclo[2.2.1]heptane-2,3-semidione. The basic geometry and numbering are as shown in Figure 6. The coupling constants calculated for the various conformations and substitutions are collected in Table II. The conformation (a) yields results which are in much better agreement with the experimental values, but this is possibly fortuitous in view of the better agreement between the conformation (b) and the geometry reported for *anti*-7-norbornenyl *p*-bromobenzenesulfonate.[39]

Table II. Observed[5] and Calculated hfsc's for the Bicyclo[2.2.1]heptane-2,3-semidiones

Position	1(4)	5(6)-*exo*	5(6)-*endo*	7-*syn*	7-*anti*
Unsubstituted					
Obsd	2.49	2.49	0.0	0.41	6.47
Calcd	1.4[a]	1.5	0.5	0.3	6.4
	1.8[b]	0.8	0.1	0.0	4.6
	1.4[c]	1.3	0.1	0.3	12.0
1-*syn*-7-Dimethyl					
Obsd	0.2[d] (2.55)	2.55	0.0	0.2[d]	3.05
syn-7-Methyl					
Calcd	1.1[a]	1.6	0.5	0.1[e]	3.2
	1.5[b]	0.8	0.1	0.3[e]	1.6
endo-5,6-Dimethyl					
Obsd	2.33	1.84	0.2[d]	0.4	6.97
endo-5-Methyl					
Calcd	1.6[a]	0.4 (1.7)	0.4[e] (0.6)	0.3	6.5
	2.2[b] (2.1)	0.2 (0.9)	0.3[e] (0.2)	0.0	4.5

[a] All values are in gauss. $\theta = 134°$, $\phi = 115°$, $D = 2.286$ A. [b] $\theta = 125°$, $\phi = 110°$, $D = 2.286$ Å. [c] $\theta = 125°$, $\phi = 110°$, $D = 2.6°$ Å. [d] $a_{CH_3}{}^{H}$, three equivalent hydrogens observed. [e] Average for $a_{CH_3}{}^{H}$, one conformation only.

Bicyclo[2.2.2]octane-2,3-semidione. Again, the basic model was constructed following the values calculated for the parent hydrocarbon; the geometry and numbering are shown in Figure 7. Coupling constants were also calculated by varying θ and D, and the results for these geometries and for the methyl-substituted structures are shown in Table III.

Good agreement with experiment is observed in the unsubstituted radical; a value of θ slightly greater than 120° would remove completely the small discrepancy. Upon alkyl substitution, it is seen that a bridgehead methyl group has little effect on all coupling constants, while an *endo*-5-methyl decreases the *exo*-5-hydrogen interaction by almost 50% and has a smaller effect on the more distant hydrogens. Both these trends are in excellent agreement with the experimental results.[5]

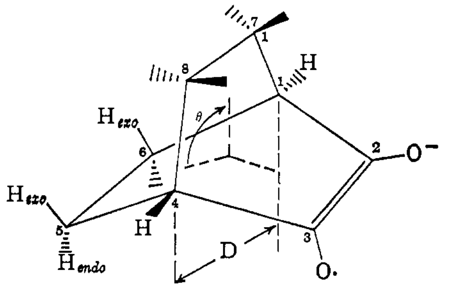

Figure 7. The geometry and numbering for bicyclo[2.2.2]octane-2,3-semidione.

Table III. Observed[5] and Calculated hfsc's for the Bicyclo[2.2.2]octane-2,3-semidiones

Position	1(4)	5,6,7,8-*exo*	5,6,7,8-*endo*
Unsubstituted			
Obsd	0.0	2.09	0.0
Calcd	0.0[a]	1.7	0.0
	0.0[b]	2.7	0.2
	0.0[c]	1.8	0.0
endo-5,6-Dimethyl			
Obsd	0.0	1.34, 1.34, 2.12, 2.12	0.0
endo-5-Methyl			
Calcd	0.0[a]	1.0, 1.6, 1.7, 1.5	0.0, 0.1[d]
1-Methyl-4-methoxy			
Obsd	0.0	2.14	0.0
1-Methyl			
Calcd	0.5[a,d] (0.0)	1.6	0.0

[a] All values are in gauss. The basic geometry was $\theta = 120°$, $D = 3.0$ Å. [b] $\theta = 130°$, $D = 3.0$ Å. [c] $\theta = 120°$, $D = 3.2$ Å. [d] $a_{CH_3}{}^{H}$, calculated for one conformation only.

Conclusion

The application of the extended Hückel theory to the calculation of long-range hfsc's gives good agreement with the experimental values considering the gross approximations made. This treatment appears particularly successful in predicting the effect of alkyl substitution and the relative magnitudes of the coupling constants.

We are currently examining the possible extension of the EH treatment to hfsc's of first row elements and refinement of the treatment of proton hf interactions.

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